MOLYBDENUM RECOVERY FROM TWO TYPES OF
DIRECT CATALYTIC COAL LIQUEFACTION PROCESSES

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INTRODUCTION

Molybdenum-containing catalysts are widely used in the petroleum refining industry for mild hydrogenation and removal of heteroatoms such as nitrogen, oxygen, and sulfur, as well as metals like nickel and vanadium. This hydroprocessing technology is being extended to upgrading of petroleum substitutes such as shale oil, tar sands, and coal liquids. But molybdenum catalysts also play an important role in several direct coal liquefaction processes.

In one type of liquefaction operation, a conventional petroleum-type $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ catalyst can be used for rehydrogenation of the recycle solvent stream. In two-stage coal liquefaction processes, the initial liquefaction step uses only natural components of the coal ash as catalysts, but the second stage employs a $CoMo/Al_2O_3$ catalyst for upgrading.

A third type of operation utilizes a $CoMo/Al_2O_3$ catalyst in the liquefaction reactor. Fresh catalyst can be added to the top of the reactor while spent catalyst can be withdrawn from the bottom. Here, the catalyst is in direct contact with the coal.

In a fourth variation, a molybdenum compound is dispersed in the coal-oil feed slurry. Carried through the liquefaction reactor, a portion of the molybdenum is recycled with solvent while the remainder goes along with the liquid product stream and then with the residue into a gasifier in the hydrogen plant. Eventually, the Mo is discharged from the plant as a component of the coal ash. Here again, the molybdenum catalyst is in direct contact with the coal although no refractory support is employed.

Coal liquefaction processes can consume large quantities of catalyst. For example, an H-Coal-type plant processing 20,000 tons of coal a day and using catalyst at a rate of 1.5 lb/ton of coal would require about 10 MM pounds of $CoMo/Al_2O_3$ a year on a once-through basis. While regeneration and improved utilization rates might reduce this amount substantially, the demand for fresh catalyst would still be sizable.

MOLYBDENUM RECOVERY PROCESSES

The investigation of molybdenum recovery methods was limited to two types of catalyst systems, one in which $CoMo/Al_2O_3$ was in direct contact with coal in the liquefaction reactor and one that employed a molybdenum compound dispersed in the coal-oil feed slurry. This work has been carried out on a laboratory scale only and has not been evaluated in pilot plant equipment.

$CoMo/Al_2O_3$ Catalyst

Laboratory studies began with "as received" spent $CoMo/Al_2O_3$ petroleum hydrodesulfurization (HDS) catalyst that contained substantial quantities of sulfur, coke, and heavy hydrocarbons. A sample of $CoMo/Al_2O_3$ catalyst from a coal liquefaction pilot unit has recently been obtained and is currently being tested to determine the effects of coal ash components such as Fe, Ca, Ti, and Si on Mo recovery.

Figure 1 shows a schematic flow diagram for the process. The chemistry involved is not unique to this operation, having been reported in numerous scientific publications and patents.

The spent coal liquefaction catalyst is first ground to approximately −100 mesh particle size to facilitate gas-solid contact in subsequent steps. Then the pulverized material is roasted in air at 600 C in a direct fired rotary kiln or fluid bed calciner to remove carbon and sulfur deposits. The calcined material is mixed with soda ash (Na_2CO_3) to obtain intimate contact. This probably can be done without cooling as the material leaves the Air Roaster. The Na_2CO_3-calcine mix is then roasted again in air at 750 C in a second rotary kiln or fluid calciner to convert molybdenum oxide (MoO_3) to Na_2MoO_4.

$$MoO_3 + Na_2CO_3 \rightarrow Na_2MoO_4 + CO_2\uparrow \qquad\qquad 1)$$
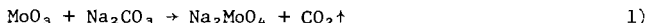
The Na_2CO_3 Roaster product is water leached at 100 C in a continuous stirred tank reactor vessel to solubilize the molybdenum. Insoluble $Co-Al_2O_3$ residue and the Na_2MoO_4 solution are readily separated by filtration. The filter cake, after washing, is ready for cobalt recovery.

The filtrate is transferred to a Mo recovery circuit and treated with calcium chloride or lime at ambient temperature to precipitate calcium molybdate which is filtered, washed, and dried.

$$Na_2MoO_4 + CaCl_2/Ca(OH)_2 \rightarrow CaMoO_4\downarrow + 2NaCl/2NaOH \qquad\qquad 2)$$
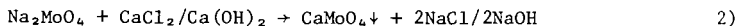
The filtrate from the Mo Precipitation Tank will probably require neutralization before discharge as a waste solution.

Laboratory scale experiments with this processing scheme have resulted in molybdenum recoveries between 90 and 95% with no cobalt contamination.

Capital and operating cost estimates for the process are shown in Table I. All costs are "order of magnitude" or "preliminary" which implies ±30%. The design assumptions used in this estimate are:

1. Spent catalyst is obtained from a 20,000 TPD or 50,000 TPD coal liquefaction plant consuming 1.5 lbs of $CoMo/Al_2O_3$ catalyst per ton of coal.

2. The composition of the spent catalyst was 10% Mo, 2.5% Co, 10% S, 10% C, with the balance Al_2O_3.
3. The plant operates 330 days/year, 24 hours/day.
4. Mo recovery is 95% in the spent catalyst plant.
5. No cost is applied to the spent catalyst.
6. No credit is taken for $Co-Al_2O_3$ nor are costs for their separation charged to Mo recovery.
7. Raw material costs are those published in Chemical Marketing Reporter, March 1, 1982.
8. Capital costs are based on March 1982 estimates using a Chemical Engineering Index of 330.

The type and size of all equipment were chosen using normal engineering estimating procedures based on the small scale lab tests. Several less conventional alternative equipment types may be suitable at significant capital economies. In addition, no attempt was made to optimize raw material or utility consumptions, which would also be amenable to economization. Eventually all equipment sizes, raw materials, and utility consumptions must be confirmed by pilot scale tests.

The cost estimates show that manufacturing costs, especially labor and associated overheads, are very sensitive to plant capacity in the 20,000 TPD to 50,000 TPD coal feed range. This suggests that a large, centrally-located catalyst processing plant servicing several coal liquefaction facilities would result in the lowest molybdenum recovery costs.

The total operating cost of $3.29/lb Mo feed shown in Table I does not include the cost to make-up the 5% Mo losses in the process. In addition, the Mo is recovered from the spent catalyst as $CaMoO_4$ which is not a suitable feed for catalyst preparation but is an acceptable material for metallurgical use. A more expensive molybdenum compound, a high purity oxide, is required for catalyst manufacture. Consequently, a cost penalty is also incurred for the reduced value of the recovered Mo. The Mo recovered as $CaMoO_4$ (95% of the starting material) has a value equivalent to a technical grade oxide ($8.62/lb Mo) and thus credits the operating cost with $8.19/lb Mo feed. The replacement Mo as a pure oxide ($9.58/lb Mo) adds $9.58/lb Mo feed to the operating cost. This results in a net additional cost of $1.39/lb Mo feed, and raises the net operating cost to $4.68/lb Mo feed. Even with a 100% Mo recovery, the current Mo pricing structure results in a cost penalty of $0.96/lb Mo feed.

Based on laboratory data, the process appears to be technically feasible but needs more definition on the effects of coal ash contamination on Mo recovery. The economics also look promising with the potential for improvement via alternate technology.

Dispersed Molybdenum Catalyst

When a molybdenum compound is dispersed in the coal-oil feed slurry, a different type of recovery process can be used. Ultimately, Mo is rejected from the liquefaction plant as a component of the coal ash. However, after passing through the liquefaction reactor and product separators, the Mo catalyst, along with unreacted coal, char, residual hydrocarbons, and the ash may be fed to a partial oxidation gasifier in a hydrogen plant. Molybdenum-containing coal ash that has been subjected to gasification conditions has not been available in quantities sufficient for adequate testing. Consequently, synthetic mixtures of coal ash from a gasification unit and Mo metal powder have been used in evaluating the Mo recovery process. The coal ash-Mo metal blend was fused to insure intimate contact of the components. After cooling, the solid melts were ground to approximately -100 mesh and mixed with soda ash (Na_2CO_3).

As shown in the schematic flow diagram for the process (Figure 2), the Mo-ash-
Na_2CO_3 mixture is roasted in air at 700 C in a direct fired rotary kiln or fluid
bed calciner. There is no need to air roast the ash before addition of Na_2CO_3
because the deleterious sulfur and carbon impurities have already been removed in
the gasifier.

The roasted mixture is slurried with water at 100 C to extract Na_2MoO_4. The ash
residue is then washed, dried and discarded. The filtrate and wash liquor contain-
ing dissolved Na_2MoO_4 and excess Na_2CO_3 are mixed and ammonia added to an NH_3/Mo
ratio of 1/1-2/1. Then sulfuric acid is added to the ammoniacal solution, main-
tained at 80-100 C, until an ammonium polymolybdate is precipitated at a pH of
1.0-3.0. Finally, the precipitate is filtered and dried. The ammonium polymolyb-
date is quite suitable for recycle directly into the coal-oil feed slurry of a coal
liquefaction process either as a solid or dissolved in a dilute ammonia solution.

Complete capital and operating cost estimates for this process are shown in Table II.
Again, all costs are ±30%. The design assumptions used in this estimate are:

1. The ash residue is obtained from a coal liquefaction plant processing
   20,000 TPD of coal with an ash content of 10%.
2. The ash residue contains 2% Mo.
3. The plant operates 330 days/year, 24 hours/day.
4. Molybdenum recovery from the ash residue is 95%.
5. Raw material costs are those published in Chemical Marketing Reporter,
   March 1, 1982.
6. Capital costs are based on March 1982 estimates using a Chemical
   Engineering Index of 330.

No attempt was made to optimize raw material or utility consumptions. Also, less
conventional alternative equipment types may be suitable at significant capital
economies. Based on laboratory scale experimentation, the process appears to be
technically feasible. However, it must be remembered that test samples were mix-
tures of coal ash and Mo metal powder. Until Mo-containing ash residue from a
gasifier becomes available, technical feasibility of the process will not be
assured.

Economic analysis (Table II) shows this Mo recovery process to be attractive, even
with high capital costs of $31 MM compared to the $11.2 MM capital costs for an
identically-sized coal liquefaction plant using $CoMo/Al_2O_3$ catalyst (Table I). The
difference is related to the large volume of ash that must be processed. For
example, a 20,000 TPD liquefaction plant processing coal with 10% ash content will
generate 2000 TPD of Mo-containing ash versus only 15 TPD of $CoMo/Al_2O_3$ spent
catalyst from the first process. In fact, the massive quantities of ash generated
set the size of the Mo recovery plant independent of the amount of Mo in the ash.
Since the concentration of Mo may vary from 0.25% up to about 8%, the total amount
of molybdenum is small compared to the amount of ash. Therefore, equipment sizes
are essentially the same for all concentrations of Mo. Figure 3 shows the manu-
facturing costs for a plant recovering Mo from the ash as a function of the initial
molybdenum concentration. Parametric curves are shown for molybdenum yield as well
as one case for a 50,000 TPD coal plant.

At any given Mo concentration in the ash, there is only a small effect of recovery
yield on the unit cost of recovery. But this does not take into account the cost
of make-up material. Recovery costs are not sensitive to plant capacity at
20,000 TPD to 50,000 TPD scales. However, process costs are very sensitive to Mo
levels in the ash and are probably prohibitive at molybdenum levels much below 1%.

SUMMARY

Molybdenum recovery from coal liquefaction processes employing CoMo/Al$_2$O$_3$ catalysts
appears to be both technically feasible and economically attractive. Costs would
be minimized if one catalyst recovery plant serviced several liquefaction facilities.
The situation is very different with liquefaction processes employing dispersed Mo
catalysts. In this case, recovery costs show little sensitivity to plant size
above 20,000 TPD coal feed because of the large quantities of ash that must be
processed. The recovery technology appears feasible but the economics are very
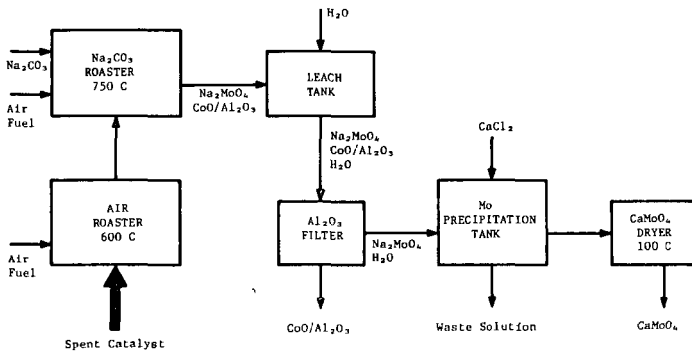sensitive to Mo levels in the ash residue.

FIGURE 1: Process Flow Sheet for the Recovery of Molybdenum
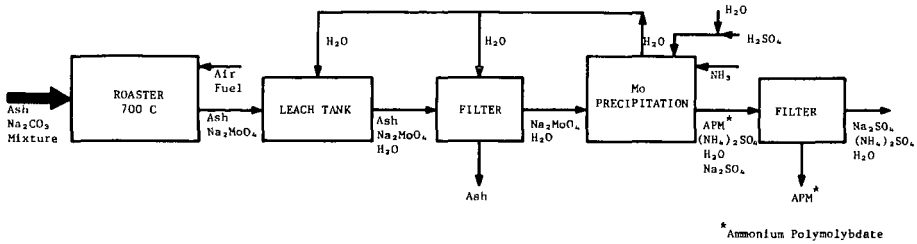from a Spent CoMo/Al$_2$O$_3$ Coal Liquefaction Catalyst

FIGURE 2: Process Flow Sheet for the Recovery of Molybdenum from a
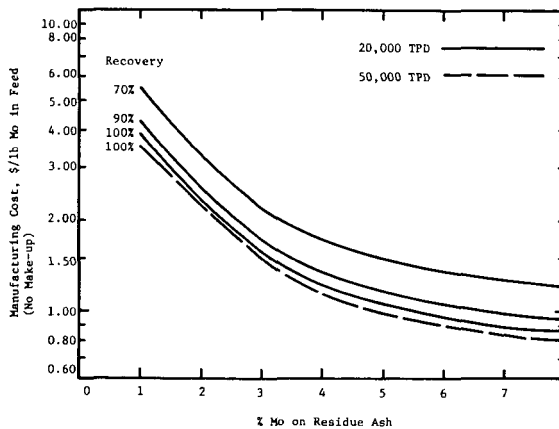Residue Ash from a Coal Liquefaction Plant

FIGURE 3: Manufacturing Costs for a Process to Recover Molybdenum
from a Residue Ash from a Coal Liquefaction Plant

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TABLE I. Capital and Manufacturing Costs For a Process to Recover Mo from a Spent CoMo/Al$_2$O$_3$ Catalyst for Coal Liquefaction

Basis: 1.5 lbs catalyst/ton coal, 95% Recovery
Catalyst Composition: 10% Mo, 2.5% Co, 10% S, 10% C, bal Al$_2$O$_3$

Coal Liquefaction Plant Capacity	20,000 TPD	50,000 TPD
Mo Plant Capital Cost	$11.18 MM	$13.87 MM
Manufacturing Costs, $/lb Mo in Feed		
Raw Materials	$0.29	$0.29
Utilities	0.12	0.12
Labor	1.96	0.78
Maintenance	0.68	0.34
Operating Supplies	0.17	0.08
Payroll Overhead	0.92	0.39
Indirect Costs	1.32	0.56
Fixed Costs - taxes, insurance	0.34	0.17
- depreciation	1.13	0.56
Total	$6.93	$3.29
Mo Make-up and Penalty Costs	1.39	1.39
	$8.32	$4.68

TABLE II. Capital and Manufacturing Costs for a Process to Recover Mo from a Residue Ash from a Coal Liquefaction Plant

Basis: 20,000 TPD coal plant
10% ash in coal
2% Mo in ash
95% Mo recovery

Mo Plant Capital Cost: $31 MM

Manufacturing Costs, $/lb Mo in Feed

Raw Materials	$1.19
Utilities	0.83
Labor	0.07
Maintenance	0.07
Operating Supplies	0.02
Payroll Overhead	0.05
Indirect Costs	0.07
Fixed Costs - taxes insurance	0.03
- depreciation	0.12
Total	$2.45
Mo Make-up Costs	0.48
	$2.93